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straints. The optical properties of most substances show their electrons to be held rather rigidly, but many of the properties of metals, and especially of metals pronouncedly electro-positive in character, indicate a high degree of electronic freedom.

It is therefore our belief that in the metals under consideration the difference between the heat capacity observed and that calculated from the regular curve, which fits the experimental curve at low temperatures, may be regarded as representing the actual heat capacity of their more loosely bound electrons. Whether these electrons are 'free' in the sense that each electron occupies a position symmetrical with respect to two or more atoms, or whether they remain attached to individual atoms, we should expect them to add to the heat capacity of the substance, provided that they are held by sufficiently weak constraints.

We have thus an entirely new method of investigating the freedom of electrons in a metal, and it is to be hoped that when further quantitative data are available a comparison of the results obtained by this method with those obtained through a study of the photo-electric effect, or the Volta effect, will prove of interest.

[1] Lewis, *J. Amer. Chem. Soc., Easton, Pa.* **29**, 1907, (1165); *Zs. anorg. Chem., Hamburg*, **55**, 1907, (200).

[2] Lewis and Adams, *Physic. Rev., Ithaca, N. Y.*, (Ser. 2), **4**, 1914, (331).

[3] Langmuir, *J. Amer. Chem. Soc., Easton, Pa.*, **38**, 1916, (2236), calls attention to the possibility that the atom in a solid may not be vibrating in simple harmonic motion and hence that the potential energy may not be equal to the kinetic energy, as has been assumed. However, if this were the case the potential energy would in all probability be less than the kinetic energy and not greater.

[4] Dewar, *London, Proc. R. Soc., A*, **89**, 158, 1913, (158).

[5] Nernst and Schwers, *Berlin Sitz. Ber. Ak. Wiss.*, 1914, (1), (255).

[6] See Lewis and Gibson, *J. Amer. Chem. Soc., Easton, Pa.*, **39**, 1917, (2554).

[7] The four highest points of Nernst and Schwers have been omitted since they appear to us to be erroneous.

THERMO-ELECTRIC DIAGRAMS ON THE P-V-PLANE

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Read before the Academy, November 21, 1917

About thirteen years ago I made an ill-directed and unfortunate attempt to analyze the electromotive force of a thermoelectric circuit, that is, to identify and explain the local e.m.f's which, taken together, give the e.m.f. of the circuit as a whole. I am now making a new attempt. I know that my present effort is more intelligently directed than the former one, and hope that it will prove to be more fortunate; but I do not claim for it finality.

I shall in the present paper discuss the matter on the assumption that the 'free' electrons within the metals are the only ones moving progressively in the maintenance of a current and the only ones taking part in thermo-electric action. For the sake of generality I shall not assume that these electrons have the same kinetic energy as gas molecules or even have the same kinetic energy in different metals at the same temperature. In fact, I shall in using the equation

$$pv = GRT, \tag{1}$$

where v is the volume of a gram of free electrons within a metal and G is the number of electrons in this gram, assume that R may be a function of T and may vary from metal to metal. I shall follow common practice in supposing n, the number of free electrons per unit volume, to be greater in some metals than in others and to increase in all metals with rise of temperature. I shall omit, as being unnecessary for a general explanation of thermo-electric action, the assumption of a specific attraction of metals for electrons.

In a detached bar of metal α, kept hot at one end and cold at the other, there is a higher free-electron pressure at the hot end than at the cold end, partly because of the greater value of n, partly because of the higher average heat energy of the electrons, at the hot end. Hence there is a mechanical tendency of the free electrons to move toward the cold end of the bar. But it cannot be said with confidence that this tendency, if unrestricted, would result in a condition of equal pressure from end to end of the bar; for it is quite possible, as I have pointed out in a previous paper,[1] that it would produce the condition of equilibrium which holds in 'thermal effusion.'

I shall make use in turn of two alternative hypothesis;

(*A*) That the mechanical tendency is toward equality of pressure, represented by the equation

$$nRT = a\ constant,$$

from end to end of the bar.

(*B*) That the mechanical tendency is toward thermal effusion equilibrium, represented by the equation

$$n\,(RT)^{\frac{1}{2}} = a\ constant,$$

from end to end of the bar.

Under neither hypothesis will there be any sufficient movement of electrons to produce an appreciable alteration of n from its natural value at any point,—that is, the value it would have at this point if the whole bar were at the temperature of this point. For the free electrons are mingled, naturally, with an equal number of positive metal ions which are not free to move through the bar, and therefore these electrons are powerfully restrained from any large movement down the pressure gradient. The proper distribution of an exceedingly small excess of them along the surface of the colder half of the bar, with a corresponding deficiency in the warmer part, is enough to balance the mechanical-pressure tendency and maintain equilibrium. Of course this equilibrium is a mobile one, individual electrons moving in either direction through any cross-section of the bar constantly, but with zero net result so long as the bar is isolated and of unchanging temperature-gradient.

The pressure gradient, and the balancing electric potential, will depend on the rate at which n increases with increase of T in this metal α. Let this rate be such that the changes of pressure and volume suffered by one gram of electrons in passing, under conditions differing only slightly from those of equilibrium, from temperature T_1 to temperature T_2, or *vice versa,* through the metal α are represented by the curve[2] $A\ D$ in figure 1.

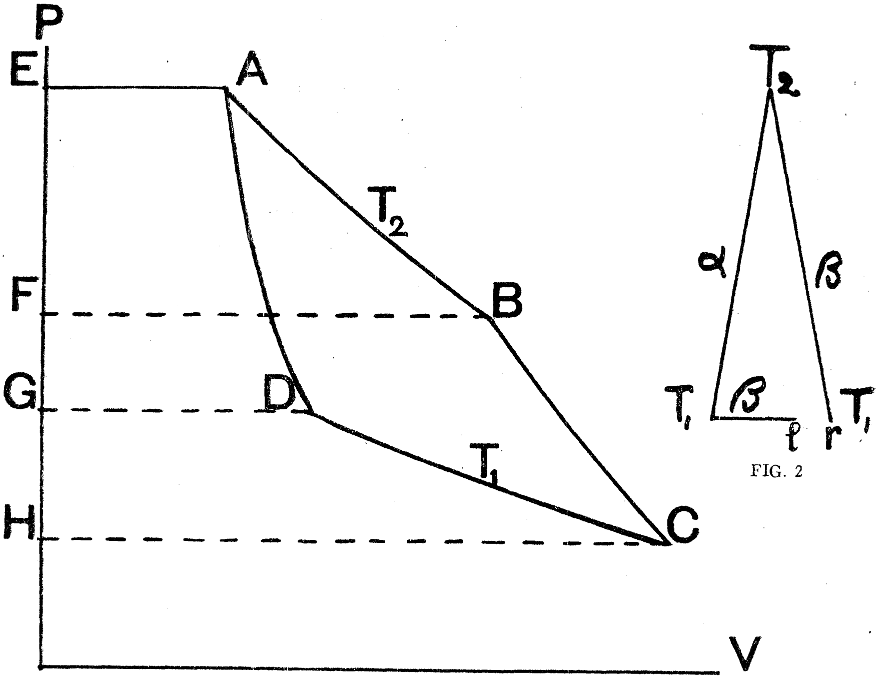

FIG. 1

FIG. 2

If this curve is steeper than the adiabatic curve of the moving body of electrons, this body will take up heat from the metal during its progress from T_1 to T_2; that is, the Thomson heat-effect in this metal will be of the same sign as that in iron. If the line is less steep than the adiabatic, the Thomson heat-effect will be of the same sign as that in copper. In lead the adiabatic line would be followed very nearly.[3]

Let the line $B\ C$ be for the metal β what the line $A\ D$ is for α.

Under hypothesis A.—In order to have electrical equilibrium within the bar, we must have

$$dp = f\, n\, dl \tag{2}$$

where f is the electrostatic force acting on a single electron in the direction of increasing T, and dl is the element of length of the bar corresponding to the change of pressure dp. Hence the decrease of negative electrostatic potential from the cold to the hot end of the bar is

$$P_1 - P_2 = \frac{1}{e}\int_0^l f dl = \frac{1}{e}\int_0^l \frac{fndl}{n} = \frac{1}{e}\int_0^l \frac{dp}{n} = \frac{1}{Ge}\int_{p_1}^{p_2} v\, dp, \tag{3}$$

where e is the electron charge, v is the volume of 1 gram of the electrons, and G is the number of electrons therein. The value of the last integral is evidently equal to the area $E\,A\,D\,G$ for the bar α and to the area $F\,B\,C\,H$ for the bar β.

Each of the lines $A\,D$ and $B\,C$ corresponds to a state of equilibrium for its metal. Let us now suppose the two metals to be joined together at the hot end while an additional piece of the metal β, at temperature T_1, is joined to the T_1 end of α, as in figure 2, leaving a gap between two pieces of β, with temperature T_1 at both l and r. We may, if it seems desirable, instead of joining the two metals directly, insert at each junction a bar, or bridge, of alloy changing in composition from pure α at the left end to pure β at the right end, the whole length being at the temperature of the α and β adjacent. See Figure 3. Through each of the bridges we shall have a gradual change of n, from the valuable proper to α to the value proper to β.

At the instant when the junctions indicated are effected there will probably be a slight movement of electrons from one metal to the other, lowering a little the electric potential of one bar as a whole and raising that of the other; but the gradient of mechanical pressure, and so the balancing gradient of electric potential, will remain sensibly unaltered in each. Along each of the isothermal bridges of alloy the general law of equilibrium will be the same as that which we have seen to hold in each of the homogeneous but now isothermal bars; that is, dp equals $fndl$. The volume-pressure changes through the bridge at T_1 will be those shown by the isothermal line $A\,B$ of figure 1; the corresponding changes through the bridge at T_1 will be those shown by the isothermal $D\,C$. The increase of negative electric potential through the bridge at T_2 from α to β will be, according to equation (3), represented by $\frac{1}{Ge} \times$ (*the area $E\,A\,B\,F$*). The corresponding increase at the T_1 junction will be $\frac{1}{Ge} \times$ (*the area $G\,D\,C\,H$*).

We still have equilibrium, the circuit being open at lr. But is the potential of the β at l equal to that of the β at r? We can answer this question readily. Starting in α (fig. 3), close to the T_2 junction, going across the bridge and then down β to r, we have as the gain of negative potential

$$P_r - P_{\alpha_2} = \frac{1}{Ge}(EABF + FBCH) = \frac{1}{Ge} \times EABCH \tag{4}$$

Starting again at the same point as before and going down α, then across the lower bridge to β, we get

$$P_l - P_{\alpha_2} = \frac{1}{Ge}(EADG + GDCH) = \frac{1}{Ge} \times EADCH. \tag{5}$$

We have, then, by subtraction

$$P_r - P_l = \frac{1}{Ge} \times ABCD. \tag{6}$$

If now we choose to connect l and r by means of some very large resistance, the current will flow from r to l through this resistance, while the conditions within α and β will remain almost unchanged. We shall have a thermo-electric current passing clockwise around the circuit of Fig. 2, or Fig. 3, and the e.m.f. maintaining this current will be $\frac{1}{Ge} \times A\,B\,C\,D$. The amount of electrical work done by a gram of electrons, *Ge* units, in passing once around this circuit is $A\,B\,C\,D$, which is, of course, equal to the mechanical work of the pressure-volume cycle through which the gram of electrons passes.

Under Hypothesis B.—In this case, as I have elsewhere shown,[1] we have, as the condition of electrical equilibrium in a detached bar with a temperature gradient,

$$dp = \tfrac{1}{2}\,p\left(\frac{dR}{R} + \frac{dT}{T}\right) + fndl. \tag{7}$$

Hence

$$P_1 - P_2 = \frac{1}{e}\int_0^l fdl = \frac{1}{e}\int_0^l \frac{fndl}{n} = \frac{1}{e}\int_{p_1}^{p_2} \frac{dp}{n} - \frac{1}{2e}\int_1^2 \frac{p}{n}\left(\frac{dR}{R} + \frac{dT}{T}\right).$$

But

$$\frac{p}{n} = RT = \frac{pv}{G},$$

and so

$$P_1 - P_2 = \frac{1}{Ge}\int_{p_1}^{p_2} vdp + \frac{1}{2Ge}\left(p_1v_1 - p_2v_2\right). \tag{8}$$

Graphically interpreted, equation (8) gives for the line AD, of figure 1 and figure 4, $P_D - P_A = \frac{1}{Ge} \times E'ADD'd'e'$, where E' is a point halfway between E and A, while D' is halfway between G and D.

For the potential difference of each of the lines $A\,B$, $B\,C$, and $D\,C$, of figure 1, we have a corresponding representation; but these areas all combined, the sum of the areas for $A\,D$ and $D\,C$ being subtracted from the sum of the areas for $A\,B$ and $B\,C$, will give, as before, $\frac{1}{Ge} \times A\,B\,C\,D$, as the net e.m.f. of the circuit.

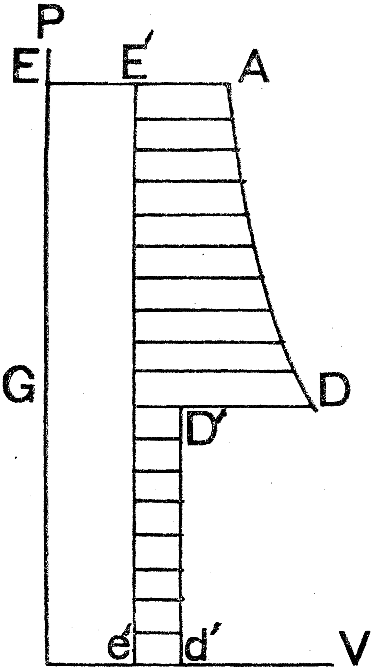

FIG. 4

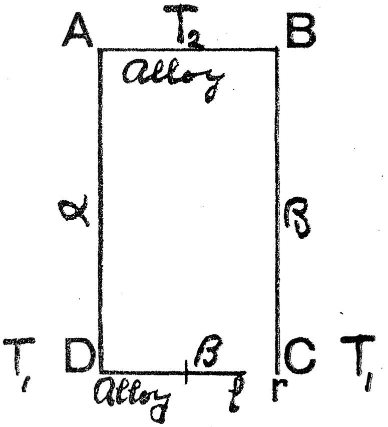

FIG. 3

If the diagram $A\,B\,C\,D$ represented the operation of an ordinary fluid, like air or steam, working in a cylinder under a piston, the path $A\,B\,C$ would represent that part of the cycle in which the fluid, expanding, does work on the piston at the expense of heat energy, while the path $C\,B\,A$ would represent that part of the cycle in which the returning piston does work in compressing the fluid. In the thermo-electric case, under the conditions which we have assumed, the path $A\,B\,C$ represents that part of the cycle in which the expanding electric fluid does work in storing up electric potential energy at the expense of heat energy, while the path $C\,D\,A$ represents that part of the cycle in which electric potential energy works to compress the electric fluid.

So far as mere expansions and contractions are concerned, we may ignore the electrical property of the circulating fluid; for the mutual electrical self-repulsion of its particles is balanced by the action of the equally numerous positive ions.

It is to be noted that no necessity has appeared in this discussion for any 'specific attraction' of either metal for electrons. Ordinary electro-static attraction and repulsion, together with the mechanical, expansive, heat-pressure of the electrons, is apparently enough to account for all that is known to occur in thermo-electric action confined to a metallic circuit. All the evidence we have to show the existence of the so-called 'specific,' or 'essential,' attraction comes from other regions of phenomena, especially from studies of thermionic emission and the Volta contact potential-difference. If such an attraction exists and is active within metals, we need not change the discussion above given except in the interpretation of P. This has here been taken as ordinary electrostatic potential. If there is an 'essential attraction' between electrons and matter having no electric charge, P will appear in the formulas just as it appears now, but it will be interpreted as what I have called in a previous paper[1] *virtual potential*, potential due to all attractions and repulsions acting on the progressive electrons.

It is of interest to observe that the e.m.f. along any part of the circuit does not, under either hypothesis (A) or hypothesis (B), necessarily correspond to the amount of heat absorbed in this part. For example, the Thomson heat absorbed along the line $A\ D$ may be positive, negative, or zero, according to the inclination of the line, while the e.m.f. of this part, represented by the area $E\ A\ D\ G$, remains always of the same sign.

The preceding discussion expressly assumes that the free electrons are the only ones which move through a metal. This is a provisional assumption only. If the associated electrons also move progressively, as I have in certain previous papers supposed them to do, the conditions of equilibrium in a detached metal bar, having a temperature-gradient, are different from those indicated in this paper. This matter I hope to discuss at another time.

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[1] Boston, *Proc. Amer. Acad. Arts Sci.*, **50,** 4 July, 1914.

[2] Great steepness of this curve does not, as one might at first suppose, indicate a very rapid increase of n with increase of T, but the contrary.

[3] That is, if the moving body of electrons that constitute an electric current obeyed the laws of a perfect manotomic gas, we should have in lead $n \propto T^{1 \cdot 5}$, very nearly.